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博　士　学　位　论　文

原位透射电镜电子束辐照诱导碳纳米管结构不稳定性研究

Study on Structural Instability of Carbon Nanotube as Induced by *In-situ* Electron Beam Irradiation in Transmission Electron Microscope

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摘 要

自从碳纳米管被发现以来，它们独特的一维管状结构和奇异的电学和力学性质引起了人们的极大关注。尤其是近年来，碳纳米管应用于纳米器件和纳米技术方面的诱人前景，促使利用电子束对它们的稳定性和相关纳米加工等进行研究成为热点研究领域。目前，利用电镜中电子束研究碳纳米管收缩、切割、焊接、改性及相关结构变化方面已有了一些报道，但是这些工作并没有把电子束辐照下碳纳米管的结构不稳定性作为一个独立课题来进行系统、定量地研究，尤其是人们只得借助现有概念并配合经典的碰撞（knock-on）机制和相关分子动力学模拟来解释和预言，而忽略了对碳纳米管结构不稳定性转变起关键作用的纳米曲率效应和电子束诱导非热激活效应。

为此，本文首先从实验上系统、定量地研究了室温时在相同电子束辐照条件下不同曲率和形态单壁碳纳米管（single-walled carbon nanotube, SWCNT）的结构不稳定性，这些 SWCNT 形态包括：（1）两端固定、轴向平直的 SWCNT；（2）两端固定、轴向弯曲 SWCNT；（3）一端固定、另端自由且轴向平直的 SWCNT；（4）一端固定、另端自由且轴向弯曲的 SWCNT；（5）一端固定、另一自由、轴向平直且末端吸附铁纳米颗粒的 SWCNT。实验结果表明，在 SWCNT 纳米曲率效应和电子束非热激活共同诱导下：1）两端固定、轴向平直的 SWCNT 表面碳原子“融蒸”导致径向收缩，收缩过程中，收缩速率随辐照不断加速，实验动力学数据非线性拟合计算表明，其表面能随曲率增大的速率远比现有理论预言的要快。当管子直径缩小到一定程度还会出现颈缩，同时表现出表面塑性流变或湿润效应；2）两端固定、轴向弯曲的 SWCNT 比两端固定、轴向平直 SWCNT 具有较大的曲率，不稳定增加，其除了发生与 1）类似的碳原子“融蒸”导致的碳管径向收缩，在轴向弯曲处因为曲率较大还会导致碳原子优先“融蒸”和向轴向平直处“扩散”而使管子整体呈轴向收缩。同时该“扩散”的碳原子一定程度上能补充轴向平直处因“融蒸”而失去的碳原子，导致碳管径向收缩减慢；3）一端固定、另端自由且轴向平直的 SWCNT 由于其顶端帽子更大的曲率，除了发生与 1）类似的碳原子“融蒸”及径向收缩外，其顶端碳原子也会优先“融蒸”和轴向“扩散”导致较

快轴向收缩，并且轴向“扩散”的原子也能及时填充轴向平直处因“融蒸”而失去碳原子的位置，能使碳管径向收缩减缓；4）一端固定、另端自由且弯曲的 SWCNT 轴向具有比 3）中一端固定、另端自由且轴向平直 SWCNT 更大曲率，更加不稳定，其“融蒸”和“扩散”速率加快，导致其轴向收缩速率比 3）中 SWCNT 更大，同样径向收缩更明显被减缓；5）一端固定、另一自由、轴向平直且末端吸附铁纳米颗粒的 SWCNT，由于铁纳米颗粒能够钝化 SWCNT 顶端，起到抑制顶端碳原子优先“融蒸”和“扩散”作用，从而使 SWCNT 轴向收缩变慢同时能导致碳管径向收缩实现。

在对 SWCNT 结构上述不稳定性研究基础上，本文进一步从实验上较为系统地研究了室温时在相同电子束辐照条件下结构更为复杂的不同形态多壁碳纳米管（multi-walled carbon nanotube, MWCNT）的结构不稳定性，这些 MWCNT 形态包括：(1)两端固定、轴向平直的 MWCNT;(2)两端固定、轴向弯曲的 MWCNT;（3）一端固定、另端自由且轴向平直的 MWCNT;（4）一端固定、另一自由末端吸附非晶碳纳米颗粒且轴向平直的 MWCNT;（5）外部管壁包裹、内嵌两根顶端帽子彼此接触 MWCNT 的复合型 MWCNT。实验结果表明，在 MWCNT 纳米曲率效应和电子束非热激活共同诱导下：（1）两端固定、轴向平直的 MWCNT 表面碳原子“融蒸”和在内壁较大曲率或表面能驱动下径向往内腔“扩散”，导致径向收缩，同时室温下电子束辐照诱导晶格缺陷不断积累，管壁层状结构断裂及非晶化，且随非晶化程度增加径向收缩加快，但随着管子内腔被碳原子填充，径向收缩又被减缓；（2）两端固定、轴向弯曲的 MWCNT 除了发生与 1）类似的管壁层状结构非晶化及径向收缩外，其轴向弯曲处表面碳原子因较大曲率而优先“融蒸”和轴向“扩散”，导致碳管整体呈轴向拉直及轴向收缩以减小表面能，同时轴向弯曲处表面轴向“扩散”碳原子一定程度上能补充轴向平直处因表面 “融蒸”而失去的碳原子而使碳管径向收缩减慢。另外我们还发现轴向弯曲处优先洋葱无序化现象；（3）一端固定、另端自由且轴向平直的 MWCNT 除了发生与 1）类似的管壁层状结构非晶化及径向收缩外，其顶端帽子因较大曲率，其表面原子优先“融蒸”和向轴向平直处“扩散”，导致碳管轴向收缩。并且轴向“扩散”的原子能及时填充轴向平直处因“融蒸”而失去的碳原子位置，能使碳管径向收缩减缓；（4）一端固定、另一自由末端吸附非晶碳纳米颗粒且轴向平直的 MWCNT 也会呈管壁层状结构非晶化和轴向收缩，但是非晶碳纳米颗粒能够一定程度钝化 MWCNT

顶端使其轴向收缩速率减慢，在非晶碳颗粒消失后，露出的 MWCNT 顶端碳原子就会快速轴向“扩散”导致碳管直径逐渐增大；（5）外部管壁包裹、内嵌两根顶端帽子彼此接触 MWCNT 的复合型 MWCNT，其两根内嵌 MWCNT 因其顶端帽子较大曲率而优先“融蒸”和轴向“扩散”，导致两管优先轴向收缩而彼此分开，但是随着轴向收缩速率减慢和包裹的外部管壁径向收缩的压力不断增大，其分开到一定距离后被挤压，彼此接近直至又连接在一起。总之，与 SWCNT 不稳定性相比，MWCNT 由于多层管壁之间相互影响，其碳原子“融蒸”和“扩散”情况更加复杂，除了发生与 SWCNT 类似的径向收缩和轴向收缩外，室温电子束辐照下其缺陷容易聚集而导致管壁层状结构非晶化，非晶化后 MWCNT 结构不稳定性呈总体增加。

论文整体研究突破了现有文献中电子束辐照效应的碰撞机制，发现了碳纳米管纳米曲率效应和电子束非热激活效应对碳纳米管结构不稳定性的关键影响。并发展了在纳米管纳米曲率效应和电子束非热激活效应驱动下的碳纳米管碳原子“融蒸”和“扩散”机制，对上述电子束辐照下多种形态碳纳米管的不稳定性进行了较全面、系统、深入的解释。论文研究除了为基于纳米管的新一代纳米器件设计制备及加工和其他相关纳米技术提供了可靠工艺参数和科学依据，同时也进一步证明了纳米曲率效应（纳尺寸“效应”）和电子束非热激活效应（“纳时间”效应）具有一定的普适性，能用来统一预言和解释能量束超快辐照下多种种低维纳米结构的不稳定性和纳米加工。

关键词：SWCNT；MWCNT；电子束辐照；电镜原位观察；纳米曲率效应；非热激活效应；非热激活“融蒸”；非热激活“扩散”；“纳尺寸”效应；“纳时间”效应

Abstract

Since carbon nanotube (CNT) was discovered, its unique one-dimensional tube structure and fantastic electrical and mechanical characters have attracted much attention. Especially, in recent years, the study of the instability and the relevant nanoprocessing of CNT through energetic electron beam (e-beam) irradiation for CNT's potential applications in nanodevice and nanotechnology has became a hot research area. To date, although the shrinkage, modifying, cutting, and jointing of CNT by e-beam irradiation have been reported, the structural instabilities at nanoscale (we called it herein as nanoinstabilities for short) of CNT under e-beam irradiation are not yet studied systematically, extensively or quantitatively as an independent topic. More importantly, in these studies, the people have had to resort to the existing concepts, in particularly, such as the classical knock-on mechanism and some related molecular dynamics simulations to predict and explain the behavior of CNT whereas the nanoscale curvature (we called it nanocurvature herein) effect of CNT and the energetic beam-induced non-thermal activation effect, which may be also key influencing factors, has usually been neglected.

For above considerations, in this thesis we first systematically and quantitatively investigated the non-thermal nanoinstabilities of single-walled carbon nanotube (SWCNT) with the following typical different curvatures under the same e-beam irradiation condition at room temperature: i) a straight SWCNT fixed in both ends ; ii) a SWCNT curved in axial direction and fixed in both ends; iii) a protruded segment of straight SWCNT; iv) a protruded segment of SWCNT curved in axial direction; v) a protruded segment of straight SWCNT but the tube caped end attached with a crystalline Fe catalyst nanoparticle. The experiments for the first time demonstrated different behaviors as driven by the nanocurvature effect of SWCNT and the e-beam non-thermal activation effect: I) with losing or escaping of its carbon atoms by the "evaporation", the straight single SWCNT fixed in both ends in Case i) shrank uniformly only in its radius and the shrinkage rate increased with the irradiation time. A nonlinear fit to kinetic data of shrinking radius illustrated that the increasing rate of surface energy with the nanocurvature was much faster than that predicted by the existing theory. When the radius of tube shrank to an atomic geometry configuration limit, the uniform shrinkage stopped and a necking initialized along with an intriguing

plastic flow and wetting ability on the tube surface; II) the SWCNT curved in axial direction and fixed in both ends in Case ii) was more instable than that in Case i) in general. In this case, the tube also shrank preferentially along the tube axial direction due to the faster "evaporation" and axial "diffusion" of carbon atoms at the axially curved site but its radial shrinkage was offset by the addition of the "diffused" carbon atoms to the sites with smaller curvature; III) the straight protruded SWCNT segment in Case iii) shrank preferentially in the axial direction from its caped end due to the faster "evaporation" and axial "diffusion" of carbon atoms from its most curved capped end whereas its radial shrinkage was offset again due to the addition of the "diffused" carbon atoms to the sites with smaller curvature; IV) compared with the straight protruded tube segment in Case iii), the protruded segment of SWCNT curved in axial direction was more instable and its axial shrinkage was faster due to its additional "evaporation" and axial "diffusion" at its axially curved site; V) In Case v), once being attached with the Fe nanoparticle, the cap end of the tube became passivated. Thus, the axial shrinkage was retarded and the radial shrinkage of the tube was enabled.

Based on the above research on SWCNT, we further studied systematically the nanoinstabilities of the more complex structure of multiple-walled carbon nanotube (MWCNT) with the following typical different curvatures under the same e-beam irradiation condition at room temperature: a) a straight MWCNT fixed in both ends; b) a MWCNT curved in axial direction and fixed in both ends; c) a protruded segment of straight MWCNT with a tube caped end; d) a similar protruded MWCNT segment but the tube caped end attached with an amorphous carbon nanoparticle; e) a complex MWCNT in which two inner MWCNTs contacted at their cap ends and were enveloped by several outer walls. The experiments revealed a series of similar nanoinstabilities of MWCNT as induced by the nanocurvature effect of MWCNT and the e-beam non-thermal activation effect: A) with its surface atom "evaporation" into surrounding space and inner wall radial "diffusion" into its tube hollow driven by a lower potential energy of carbon atoms of its inner walls, the straight single MWCNT fixed in both ends in Case a) shrank gradually in its radius. Nevertheless, during the irradiation, the continuous accumulation of defects and breakdown of the tube wall structure at room temperature would lead to amorphozation of the shell structure and the amorphization could speed up the shrinkage. Furthermore, it was also observed that the shrinkage slowed down again once the inner tube hollow was fully filled with

carbon atoms; B) the MWCNT curved in axial direction and fixed in both ends in Case b) would become amorphized and shrank in its radius as well. But the carbon atoms on tube surface as curved in axial direction preferentially “evaporated” and axially “diffused” to tube surface of a smaller curvature, which resulted in straightening of the tube and thus a shrinkage of tube in the axial direction to reduce the tube surface energy. At the same time, the axial “diffused” atoms could also offset the radial shrinkage of tube. In this course, we also observed that the tube site curved in axial direction preferentially amorphized due to its larger curvature; C) the protruded segment of straight MWCNT in Case c) showed similar amorphization and radial shrinkage whereas the carbon atoms in its most curved caped end preferentially “evaporated” and axially “diffused” to sites of a smaller curvature, which resulted in a shrinkage in the axial direction. Also, the axial “diffused” atoms could offset the “vapored” atoms of tube wall and thus the radial shrinkage of tube; D) the similar protruded MWCNT segment but the tube caped end attached with a amorphous carbon nanoparticle in Case d) also gradually amorphized and axially shrank, but the amorphous carbon nanoparticle showed a passivation effect on the cap end of the tube and thus an ability to retard the axial shrinkage. However, after the amorphous carbon nanoparticle disappeared via “evaporation” of atoms, the faster axial shrinkage resumed; E) For the complex MWCNT in Case e), the two inner MWCNTs also shrank axially preferentially from their most curved caped ends and separated from each other due to the preferential “evaporation” and axial “diffusion” of atoms at the caped ends. On the other hand, as the radial pressure from the out walls which enveloped the inner tubes increases with the radial shrinkage of the out walls, the two cap ends of the inner tubes were extruded to come close to each other and finally touched again. In general, compared the nanoinstability of SWCNT, that of MWCNT was relatively weaker and more complicated which involved not only “evaporation” and “diffusion” of surface atoms similar to these occurred in SWCNT but also the atom transportation and defect creation and annihilation in between the inner walls. In this way, MWCNT showed the amorphization due to the continuous accumulation of defects and breakdown of the tube wall structure at room temperature in addition to the similar typical structural changes as observed in SWCNT. More notably, this amorphization could enhance the nanoinstability of MWCNT.

The overall thesis research not only demonstrated a series of novel nanoinstabilities and nanoprocessings of CNT as induced by e-beam irradiation. The

research has also broken through the existing knock-on mechanism employed in the current literature and revealed that a novel nanocurvature effect of CNT and a novel e-beam-induced non-thermal activation effect controlled the nanoinstabilities of CNT. In particular, the non-thermal carbon atoms “diffusion” and “evaporation” mechanisms as driven by the nanocurvature effect and the e-beam non-thermal activation effect were developed and could well explain all the observed e-beam-induced nanoinstabilitiy phenomena of CNT. In doing so, the research not only provided some reliable processing parameters and the scientific basis for the design, fabrication, and processing of CNT-based nanodevices and nanotechnologies of new generation, the thesis also further confirmed that the nanocurvature effect (“nanosize” effect) and the energetic beam-induced non-thermal activation effect (“nanotime” effect) could be widespread phenomena in low dimensional nanomaterials (LDNs) and may predict and explain nanoinstabilities and nano processing of different kinds of LDNs under the energtic beam irradiation.

Key words: Single-walled carbon nanotube; multiple-walled carbon nanotube; electron beam irradiation; in-situ observation; nanocurvature effect; beam-induced athermal activation; non-thermal “vaporization”; non-themal “diffusion”; “nanosize” effect; “nanotime” effect

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第一章 绪论

1.1 电子束辐照下碳纳米管不稳定性的研究背景和意义

纳米科学技术的基本内涵是指在纳米尺寸范围内认识和改造自然，通过直接操纵和安排原子、分子创造具有特定功能的新的材料或结构。自 20 世纪 90 年代以来，纳米科学技术已逐渐成为全世界材料、物理、化学、生物、力学等多学科的研究热点及前沿，同时也将成为 21 世纪材料技术的核心。正如钱学森院士所预言："纳米左右和纳米以下的结构将是下一阶段科技发展的特点，会是一次技术革命，从而将是 21 世纪的又一次产业革命。"

低维纳米材料是纳米科学科技的基础和先导，在成为世界各国纳米技术发展热点的同时，它的发展和应用也面临许多挑战。具体而言，低维纳米材料虽然在动力学上处于亚稳态，但是因受自身尺寸的限制（通常仅为几十纳米甚至几个纳米），即在空间上被高度限制，尤其是在表面纳米曲率效应影响下，其原子从内到表面会逐渐失去对称性和平移性或偏离其平衡态，从而导致整体结构呈现出一种内禀热力学不稳定性[1-3]。因此，在传统固体物理和统计热力学的平衡和稳定基础上研究得到的传统大块材料的性质，可能完全不适用于具有内禀热力学不稳定性处于亚稳态的低维纳米材料，从而对人们的传统观念提出了挑战。比如，金膜厚度减少到几个或几十纳米时，其德拜（Debye）温度显著降低[4]；锡丝直径减小到十几纳米时，其熔化温度也显著降低[5]。进一步讲，这些非平衡或亚稳定的低维纳米材料和结构要实现最终的器件化、功能化和实用化，不仅要面临纳米器件功能稳定性和使用寿命的挑战，而且在利用能量束（电子束、离子束或激光束等）辐照对这些低维纳米材料和结构进行必要地、有目的性地精确可控纳米加工的过程中，它们的稳定性问题必须得到研究和揭示。

能量束中的电子束（尤其是高分辨透射电镜中单色性好且稳定性高的场发射电子束）作为辐照研究工具具有离子束和激光束等其他能量束所没有的优点：它是目前唯一能高分辨观察材料纳米甚至原子结构的能量束。另外，电子束一般不会给被辐照材料引入一些外来的杂质原子而影响实验结果的分析，而且它还可以较容易聚焦到纳米甚至纳米尺度以下范围并对纳米材料进行精确可控的纳米加工等。因此，高分辨透射电镜中的电子束成为科研工作者研究低维纳米材料不稳定性或进行纳米加工的首选辐照工具。研究和揭示电子束辐照下低维纳米材料的

稳定性问题，必须先理解电子束与低维纳米材料的交互作用过程。在电子束与低维纳米材料交互作用过程中，材料尺寸和能量沉积分别在空间和时间上可以被高度限制，这时，其与材料交互作用除了会产生晶体常规缺陷、非晶化、晶化和各种相变外，还会表现出许多与常规理解不同的性质。首先，电子束的能量沉积速率可以非常快，能够在很短的时间内非热激活诱导材料“点阵”失稳，导致材料不断从一个亚稳态向另一个亚稳态转变。例如，电子束辐照诱导硅中纳米孔持续收缩和纳米孔周边材料优先非晶化[2, 6, 7]；其次，电子束辐照过程中的能量沉积速率非常快时，可在很短的时间内非热激活诱导瞬态塑性流变(plastic flow)或“软化”现象。例如，加速电压为 200 kV 的电子束辐照下两端固定的单壁碳纳米管径向收缩和颈缩到一定程度时会出现表面塑性流变或湿润效应现象[8, 9]。如果仅仅通过热激活，即使加热到 1000℃，这些结构也不会出现塑性流变[10]；再次，聚焦电子束的能量可高度局域化，使沉积到材料辐照区域的能量来不及向辐照区域周围传递能量，从而导致材料高度局域化的“融化”、“融蒸”或“离削”[7,11]。例如，高强度电子束聚焦辐照下可在晶态硅纳米线上打出直径仅为 1.5nm 的纳米孔，切割出 2nm 宽度的纳米缝，而周边的材料几乎不受影响[12]；聚焦电子束也可以对单壁和多壁碳纳米管进行纳米精确加工[13-15]，它甚至可以聚焦到 1Å，精确地对碳纳米管中的单个碳原子进行加工[16]等。综上所述，超快电子束与低维纳米材料的交互作用因其非平衡、极度局域和超快限制，本质上不同于传统意义上的能量诱导大尺度材料的结构转变[7]。因此，我们必须从非平衡、极度局域和超快限制的观点出发，突破宏观固体物理、统计物理等传统观念的局限来研究和揭示低维纳米材料在电子束辐照下的稳定性问题，以期建立新的低维纳米结构不稳定性学科体系，为确定新一代纳米器件结构制造加工及性能稳定提供科学依据。

具体而言，本论文选择碳纳米管作为低维纳米材料的典型代表来进行电子束辐照研究。其主要原因如下：首先从结构而言，自从单壁和多壁碳纳米管（milti-walled carbon nanotube, MWCNT）被发现[17-19]以来，它们独特的一维管状结构及其导致的奇异的电学和力学性质等引起了人们的极大关注。尤其对于单壁碳纳米管（single-walled carbon nanotube, SWCNT）而言，它具有最小的纳米直径（单位长度原子数量最少）和最简单的单层结构，可以为我们从电子束辐照诱导低维纳米材料结构变化规律中寻找纳米效应影响范围提供最便捷的潜在极限直径窗口，而且，SWCNT 管壁外表面张应力（类似于纳米粒子）和内表面压应